1.0 | 4.5 | 2.8 | 2.5
5.0 | 3.2 | 2.2
5.6 | 3.6
1.1 | 4.0 | 2.0
1.8
1.25 | 1.4 | 1.6

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17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

The findings in this report are not to be constructed as an official position of the Department of the Air Force, unless so designated by other authorized documents.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Electron production; electron attachment; electron diffusion; charge recombination; electron conduction current; negative ion; electron-swarm; electrical discharge; opening switches; electron attaching gas; excimer laser; parallel-plate drift-tube apparatus; computer modeling.

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The electron attachment rate constants of SO_2, CS_2, and $SOCl_2$ in buffer gases of Ar, N_2, and CH_4 were measured at various E/N by a parallel-plate drift-tube electron-swarm technique. The initial electron-swarm was produced by irradiation of cathode with excimer laser. The electron attachment processes for the electronegative gases studied were investigated. The transient increase of electron conduction current by photoelectron-detachment of negative ions in the discharge medium of $SOCl_2$ in N_2 was observed. This switching is useful for the development of opening switches.

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Annual Scientific Report for Grant No. AFOSR-82-0314
Covering the Period from 1 August 1985 to 31 July 1986

ELECTRON PRODUCTION, ELECTRON ATTACHMENT, AND CHARGE RECOMBINATION PROCESS IN HIGH PRESSURE GAS DISCHARGES

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I. INTRODUCTION

This annual report covers the period from August 1, 1985 to July 31, 1986 for the research project under Grant No. AFOSR-82-0314. The processes for electron production, electron attachment, and charge recombination in high pressure gaseous mixtures were investigated in this research program. The information obtained from this program is currently needed for the development of various electrical switching devices as well as for the understanding of basic phenomena in plasma physics.

Electrical switching devices, for example, high repetition-rate discharge switches, opening switches, radiation or e-beam controlled switches, are needed for the development of high power lasers, fusion experiment, magnetic energy storage system, as well as particle beam experiment. High pressure gaseous dishcarges are often involved in these switching devices. Every discharge switch requires special characteristics pertinent to the pulse rise time, decay time, discharge stability, discharge uniformity, and current density. These characteristics are determined by the electron transport parameters of a gas mixture, such as electron drift velocity, electron attachment, detachment and ionization coefficients as well as charge recombination rates. Thus, for the design of various discharge switches, these electron transport parameters need to be well studied. This research program provides these basic data for the development of various discharge switches.

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In addition to measuring fundamental data for practical applications, we also develop new techniques for laser-controlled electrical switching. It has been observed that the electron conduction current in a gaseous discharge medium can be enhanced by photoelectron-detachment of negative ions. The electron conduction current can also be reduced by the optically-enhanced electron-attachment process. The observed current switching can, in principle, be applied to develop diffuse-gaseous-discharge opening swtiches.

II. RESEARCH ACCOMPLISHMENTS

The electron transport parameters in high pressure buffer gases were measured with a parallel-plate drift-tube apparatus. Electrons were initially produced by irradiating the cathode with an intense excimer laser pulse. The electric field produced by applying a negative high voltage on the cathode was used to drift the electrons. The transient voltage pulse induced by electron motion between the electrodes was monitored by a digitizer and stored in an IBM XT microcomputer. The electron attachment rate was obtained from the ratio of the amplitudes of transient pulses with and without a gas attacher in the buffer gas. The electron drift velocity and the electron diffusion coefficient were obtained by analyzing the time profile of transient pulse.

In this period, the switching of electron conduction current by photoelectron-detachment and photodissociation processes was also observed in the dsicharge medium of $SOCl_2$ in N_2, where a negative point-to-plane corona discharge was used. Results

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accomplished in this period are described below:

1. Electron Attachment Coefficients of SO_2

The electron attachment rate constants of SO_2 in buffer gases of Ar, N_2, and CH_4 were measured as a funciton of E/N. The electron attachment rate constant of SO_2 in Ar increases with E/N, and it is independent of Ar pressure, indicating that the electron attachment is due to the dissociative attachment process. The characteristic that the electron attachment rate increased with E/N is desirable for the design of opening switches.

For the SO_2-N_2 and SO_2-CH_4 gas mixtures, the electron attachment rates decrease with increasing E/N and increase with increasing buffer gas pressure. The electrons attachment to SO_2 in N_2 and CH_4 is attributed to the Bloch-Bradbury two-step three-body nondissociative attachment process. The mean electron energy in the N_2 or CH_4 buffer gas is lower than 1 eV, electrons do not have sufficient energy for the dissociative attachment process.

The results for the electron attachment of SO_2 in various buffer gases are reported in more detail in a paper attached as Appendix A, which has been published in the Journal of Chemical Physics.

2. Electron Attachment Coefficients of CS_2

The electron attachment coefficients of CS_2 in the buffer gases of N_2 and CH_4 were measured as a function of E/N. In both N_2 and CH_4 buffer gases, the electron attachment rates of CS_2

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increase with increasing CS_2 and buffer gas pressures and decrease with increasing E/N. This attachment process is attributed to the Bloch-Bradbury two-step three-body nondissociative attachment process. The collisional-stabilized rate for the "temporary" negative compound ion of CS_2^{-*} by various gases (CS_2, N_2, and CH_4) were also investigated.

The results for the electron attachment of CS_2 in various buffer gases are reported in the paper attached as Appendix A.

3. Electron Attachment Coefficients of $SOCl_2$

It has been demonstrated that the conduction current in a corona discharge of $SOCl_2-N_2$ mixture can be switched (increased and decreased) when the gas medium is irradiated by ArF laser photons. This observation is, in principle, useful for the development of laser-controlled opening switches. The electron attachment rates for $SOCl_2$ in various buffer gases are needed for such application.

The electron attachment coefficients of $SOCl_2$ in buffer gases of Ar, N_2, and CH_4 were measured as a function of E/N. For $SOCl_2$ in Ar, the electron attachment rate constant is maximum at E/N = 4 Td. For $SOCl_2$ in N_2 and CH_4, the electron attachment rate constants decrease with increasing E/N (1-15 Td). For every gas mixture studied, the electron attachment rate constant is independent of buffer gas pressure, indicating that the electron attachment to $SOCl_2$ is due to a dissociative electron-attachment process. The electron attachment processes in various gas mixtures were investigated.

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The results for the electron attachment of $SOCl_2$ in various buffer gases are reported in more detail in a paper attached as Appendix B, which has been accepted by the Journal of Chemical Physics for publication.

4. Switching of Conduction Current in the Discharge Medium of $SOCl_2$

The transient current in a negative point-to-plane corona discharge of $SOCl_2$-N_2 mixture produced by ArF laser pulse was investigated. The experimental apparatus is shown in Fig. 1. It has been observed that the transient current increases initially because of the increase of conduction electrons that are produced from the photoelectron-detachment of negative ions (SO^-, Cl^-, Cl_2, $SOCl^-$, etc) in the discharge medium by laser photons; and the transient current decreases later because of the increase of electron attachment rate by the photofragments (e.g. Cl, Cl^*, SO, SO^*) produced from laser dissociation of $SOCl_2$. As an example, the transient current pulses at various $SOCl_2$ pressure are shown in Fig. 2. Both of the amplitudes and duration of the transient current are being investigated as a function of [$SOCl_2$], laser energy, and laser beam size.

The results for the current switching in the discharge medium of $SOCl_2$ in N_2 will be submmerized in a paper and submitted to a scientific journal for publication. After this paper is prepared we will continue to pursue this type of experiment with different electronegative gases (e.g. SF_6) in the next funding period.

7

H.V.
0-(-30)KV

5.6 MΩ

Insulator

Gas In

Aperture

Excimer Laser

Window

Laser Energy Meter

Pump

MKS Baratron Manometer
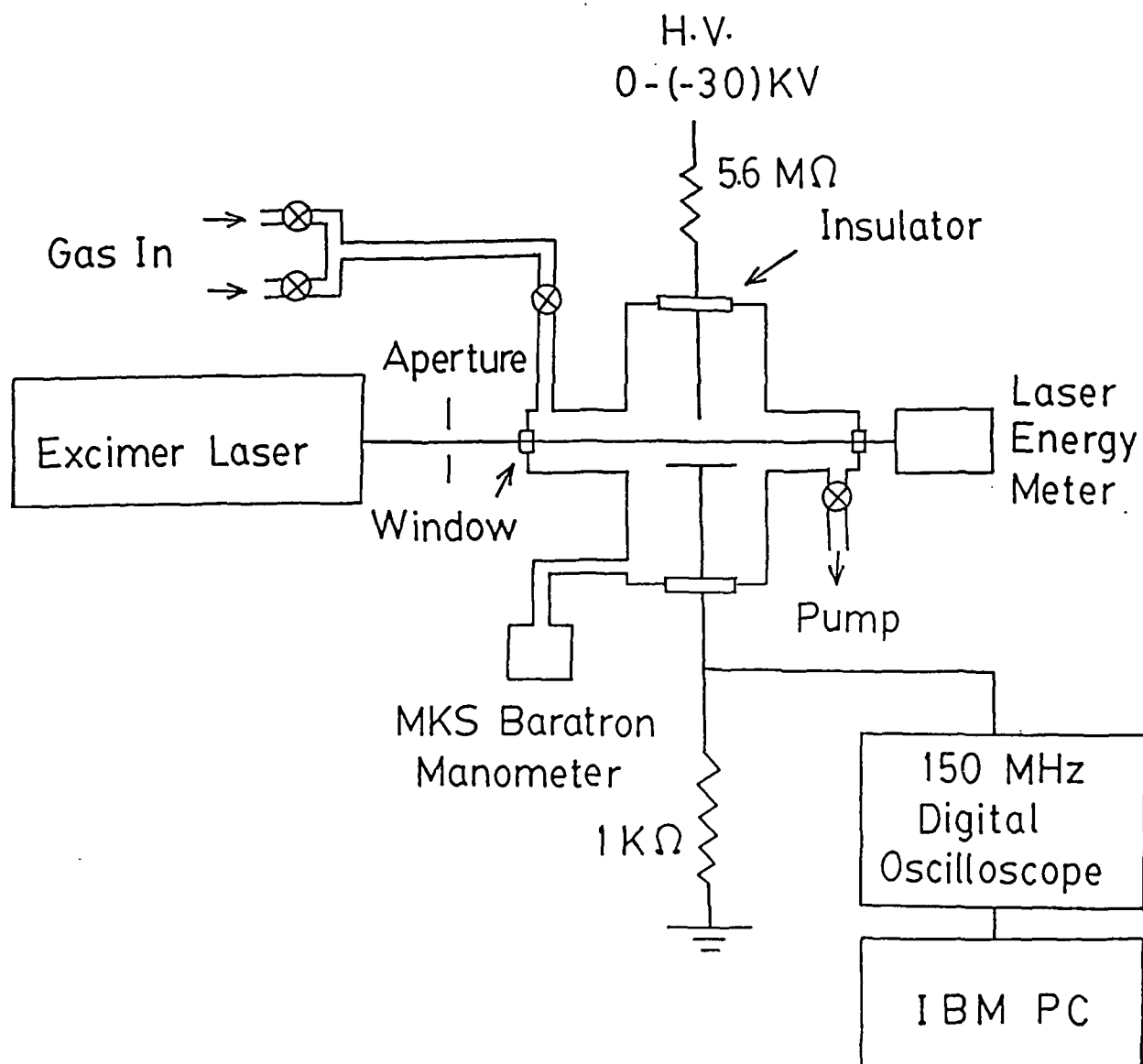
1 KΩ

150 MHz Digital Oscilloscope

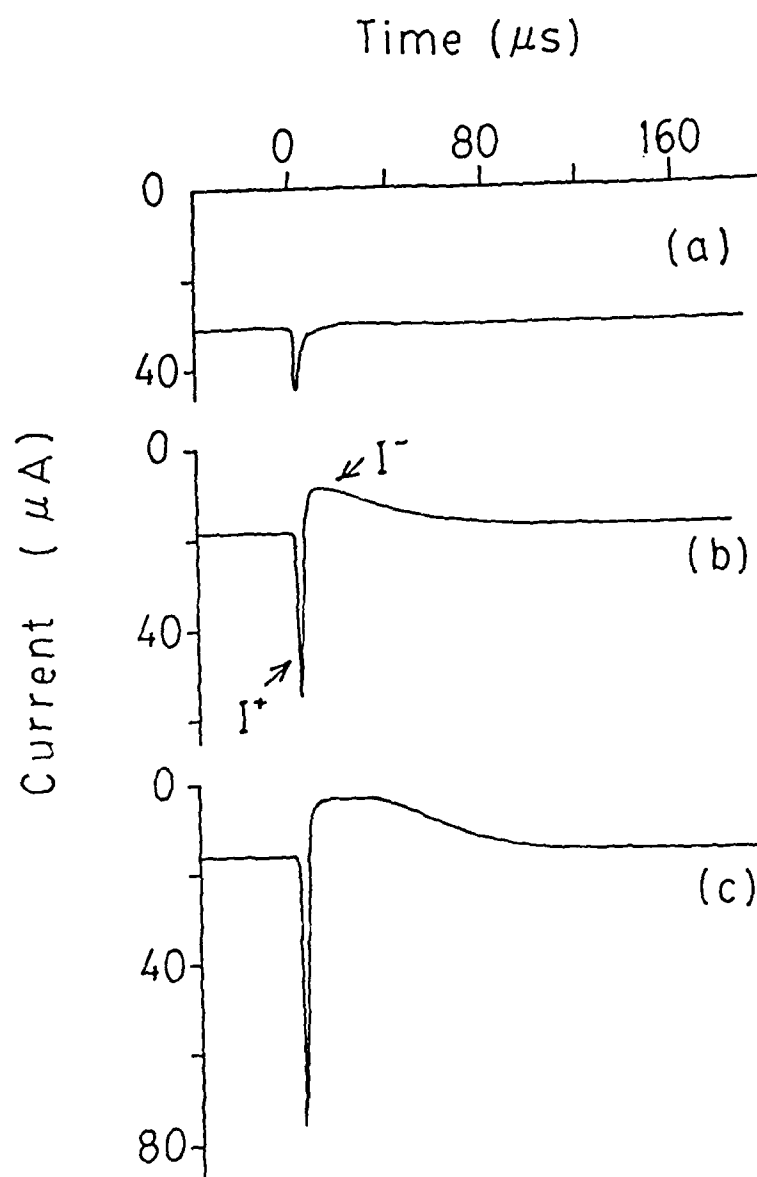IBM PC

Fig. 1.   Schematic diagram for experimental apparatus.

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Fig. 2. The transient current waveforms after the discharge medium was irradiated by an ArF laser pulse. The partial pressures of $SOCl_2$ were (a) 0, (b) 0.8, and (c) 3.4 mtorr, the laser energy was 1.5 mj/pulse, the laser beam diameter was 6 mm, the applied voltage was −0.75 kV, and the N_2 pressure was about 26 torr. I^+ and I^- indicate the current increase and decrease from the DC current level (about 18 μA), respectively.

III. CUMULATIVE PUBLICATIONS AND PRESENTATIONS

1. "Two-Photon-Ionization Coefficients of Propane, 1-Butene, Methylamines" L. C. Lee and W. K. Bischel, presented at the 12th International Conference on the Physics of Electronic and Atomic Collisions, Gatlinburg, TN, July 15-21, 1981.

2. "Electron Attachment and Charge Recombination Following Two-Photon-Ionization of Methylamines" L. C. Lee and W. K. Bischel, presented at the 34th Gaseous Electronics Conference, Boston, MA, October 20-23, 1981.

3. "Two-Photon-Ionization Coefficients of Propane, 1-Butene, and Methylamines" L. C. Lee and W. K. Bischel, J. Appl. Phys. 53, 203 (1982).

4. "Electron Ionization and Attachment Processes in Diffuse Discharges" L. C. Lee, presented to the Workshop on Optical Control of Diffuse Discharges, Eugene, OR, December 2-3, 1982.

5. "Diffusion of Electrons in Gases Under Electric Field" F. Li and L. C. Lee, presented at the 1983 Annual Meeting, APS Division of Electronic and Atomic Physics, Boulder, CO, May 23-25, 1983.

6. "Electron Longitudinal Diffusion Coefficients in Ar" F. Li and L. C. Lee, presented at the 36th Gaseous Electronics Conference, Albany, NY, October 10-14, 1983.

7. "Space Charge Effect on the Electron Kinetics Occurring in Atmospheric Gas Pressure" L. C. Lee and F. Li, presented at the 1984 IEEE International Conference on Plasma Science, St. Louis, MO, May 14-16, 1984.

8. "Shortening of Electron Conduction Pulses by Electron Attachers O_2, N_2O and CF_4" L. C. Lee and F. Li, J. Appl. Phys., 56, 3169 (1984).

9. "Electron Attachment to C_3F_8 in High Pressure Buffer Gases" W. C. Wang and L. C. Lee, presented at the DEAP Meeting, American Physical Society, Norman, OK, May 29-31, 1985.

10. "Electron Attachment to H_2O in Ar, N_2, and CH_4 in Electric Field" W. C. Wang and L. C. Lee, J. Appl. Phys. 57, 4360 (1985).

11. "Shortening of Electron Conduction Pulses by Electron Attacher C_3F_8 in Ar, N_2, and CH_4" W. C. Wang and L. C. Lee, J. Appl. Phys. 58, 184 (1985).

12. "Shortening of Electron Conduction Pulses by Electron Attachers" L. C. Lee and W. C. Wang, presented at the IEEE Pulsed Power Conference, Arlington, VA, June 10-12, 1985.

13. "Electron Attachment to H_2O, SO_2, and C_3F_8 in Ar, N_2, and CH_4" W. C. Wang, M. A. Fineman and L. C. Lee, presented at the XIV International Conference on the Physics of Electronic and Atomic Collisions, Palo Alto, CA, July 24-30, 1985.

14. "Electron Production by Photoionization of CS_2 and SO_2 at 193 nm" L. C. Lee and W. C. Wang, presented at the Thirty-Eighth Annual Gaseous Electronics Conference, Monterey, CA, Oct. 15-18, 1985.

15. "Electron Attachment to SO_2 and CS_2 in Ar, N_2 and CH_4" W. C. Wang and L. C. Lee, presented at the Thirty-Eighth Annual Gaseous Electronics Conference, Monterey, CA, Oct. 15-18, 1985.

16. "Two-Photon-Ionization Coefficients of CS_2, SO_2, and $(CH_3)_3N$" W. C. Wang and L. C. Lee, J. Appl. Phys. <u>58</u>, 3295 (1985).

17. "Electron Attachment Rate Constants of SO_2 and CS_2 in Ar, N_2. and CH_4 at varied E/N" J. Chem. Phys. <u>84</u>, 2675 (1986).

18. "Electron Attachment Rate Constants of $SOCl_2$ in Ar, N_2 and CH_4" W. C. Wang and L. C. Lee, presented at the Joint Meeting of the DAMO and DCP of the American Physical Society, Eugene, OR, June 18-20, 1986.

19. "Switching of Conduction Current by Photodetachment and Photodissociation Processes Occurring in the $SOCl_2$-N_2 Gas Mixture" W. C. Wang and L. C. Lee, accepted for presentation at the Thirty-Ninth Annual Gaseous Electronics Conference, Madison, WI, October 6-10, 1986.

20. "Electron Attachment to $SOCl_2$ in Ar, N_2, and CH_4" W. C. Wang and L. C. Lee, J. Chem. Phys. to be published Dec 15, 1986.

21. "Switching of Electron Conduction Current by Molecular Photoelectron Detachment and Photodissociation Process" submitted to SPIE, Optoelectronics and Laser Applications in Science and Engineering, Los Angeles, CA, Jan. 11-16, 1987.

IV. PERSONNEL INVOLVED IN THIS RESEARCH

1. Principal Investigator:
   Dr. Long C. Lee, Professor of Electrical & Comptuer
   Engineering

2. Research Associates:

   Dr. W. C. Wang

3. Students:

   Mr. Dan Diehl
   Mr. Robert Tahimic
   Mr. F. Mehran
   Ms. M. Waxman

V. INTERACTIONS

1. We have sent our papers to Dr. A. H. Guenther at the Air
   Force Weapons Laboratory, Dr. Alan Garscadden at the Air
   Force Wright Aeronautical Laboraotry, Dr. M. Gundersen at
   the University of Southern California, Dr. J. T. Moseley at
   the University of Oregon, Dr. Bob Reinovsky at the Air Force
   Weapons Laboratory, and Dr. S. K. Srivastava at the Jet
   Propulsion Laboratory. We appreciate the useful comments
   and suggestions received from them.

2. The results obtained in the current funding period had been
   presented at (i) the Thirty-Eighth Annual Gaseous
   Electronics Conference, Monterey, CA, Oct. 15-18, 1985; (ii)
   the APS Joint Meeting of The Division of Atomic Molecular
   and Optics Physics and The Division of Chemical Physics,
   Eugene, OR, June 18-20, 1986.

3. To participate in the workshop on "Research Issues in Pulsed
   Power Conditioning" held at the University of Southern
   California, Los Angeles, December 3-4, 1985.

Appendix A

Electron Attachment Rate Constants of

SO_2 and CS_2 in Ar, N_2, and CH_4 at Varied E/N

Electron attachment rate constants of SO_2 and CS_2 in Ar, N_2, and CH_4 at varied E/N

W. C. Wang and L. C. Lee

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The electron attachment rate constants of SO_2 and CS_2 in the buffer gases of Ar, N_2, and CH_4 (150 to 530 Torr) at various E/N (1–16 Td) were measured by a parallel-plate drift-tube electron-swarm technique. The electrons were produced by irradiating the cathode with KrF laser photons. For the SO_2–Ar mixture, the electron attachment rate constant of SO_2 increases with increasing E/N and is independent of Ar pressure. For SO_2 in N_2 and CH_4, the electron attachment rates decrease with increasing E/N and increase with increasing buffer gas pressure. For CS_2 in N_2 and CH_4, the electron attachment rates increase with increasing CS_2 and buffer gas pressures and decrease with increasing E/N. The electron attachment to SO_2 and CS_2 in the buffer gases of N_2 and CH_4 is a three-body process. The collisional-stabilized rates of "temporary" negative compound ions SO_2^- * and CS_2^- * by various gases are investigated.

I. INTRODUCTION

Recent advances in pulsed-power technology require[1] opening switches for developing a magnetic energy storage system whose energy density is much higher (10^2–10^3 times) than the capacitive system.[2] An opening switch requires a fast decay of the conduction current which may be achieved by attaching electrons to electronegative gases mixed in a buffer gas.[1] The electron attachment rates for various gas mixtures are thus of interest in practical applications as well as in basic understanding of electron attachment processes as indicated in recent electron-swarm experiments.[3] In this paper, the electron attachment processes and rate constants for SO_2 and CS_2 in Ar, N_2, and CH_4 are reported.

Electron attachment to SO_2 was first studied by Bradbury and Tatel[4] and later by several other authors[5–10] either in pure SO_2 or in various SO_2 mixtures. In pure SO_2, Lakdawala and Moruzzi[5] and Schlumbohm[6] observed that the electron attachment rate constant of SO_2 had a pressure dependence and they attributed it to the three-body nondissociative attachment process. The attachment rates of SO_2 were observed to be dependent on buffer gas pressure by Bouby *et al.*[7] for the buffer gases of N_2, CO_2, C_2H_4, and CH_3OH and by Rademacher *et al.*[8] for N_2 and C_2H_4. The electron attachment to SO_2 in various gas mixtures was attributed to the three-body nondissociative attachment process. For the SO_2–Ar mixture, the dissociative attachment process is dominant.

There is very little information available for the electron attachment process of CS_2. To the best of our knowledge, the nondissociative electron attachment rate constant of CS_2 has not been reported. CS_2^- is known to be a stable negative ion, because CS_2 has a positive electron affinity.[11,12] In fact, it has been observed in several charge-transfer reactions such as: (i) collisional ionization of alkali atoms[12]; (ii) charge transfer from highly excited Rydberg states of Kr atom[13]; (iii) charge transfer from negative ions[14]; and (iv) charge transfer from the dissociative negative ion fragments of CS_2.[14,15]

However, there are no reports on the observation of direct electron attachment to CS_2. Due to a large nuclear deformation from CS_2 to CS_2^-,[12] the probability for direct attachment of slow electrons to CS_2 may be small.

In this experiment, a parallel-plate drift-tube electron-swarm technique[16–18] was applied to measure the electron attachment rates of SO_2 and CS_2 in Ar, N_2, and CH_4 at various E/N. The E/N can be converted to the mean electron energy using the known electron energy distribution function.[3] The attachment processes in SO_2 and CS_2 are explainable by the Bloch–Bradbury two-step three-body attachment mechanism.[19]

II. EXPERIMENT

The experimental setup has been discussed in detail in previous papers.[16–18] In brief, the gas cell is a 6 in. six-way aluminum cross. The electrodes are two parallel uncoated stainless steel plates of 5 cm in diameter and 3.6 cm apart. The electron swarm was produced by irradiation of the cathode with KrF (Lumonics model 861S) laser beam which has a pulse duration of about 10 ns. An ArF laser is not used here, because it can ionize CS_2 and SO_2 by two-photon process,[20] and the electrons produced in the gas phase will perturb the electron attachment measurements. The energy of the laser pulse was monitored by an energy meter (Scientech model 365). A negative high voltage was applied to the cathode. The conduction current induced by the electron motion between the electrodes was observed as a transient voltage pulse across a resistor (100–2000 Ω) connecting the anode to ground. The transient pulse was monitored and stored by a 275 MHz storage oscilloscope (HP model 1727A) and was photographed for permanent record.

The gas pressure in the gas cell was maintained constant in a slow flow system (flow rate about 20 cm³ STP/min). The gas pressure was measured by an MKS Baratron manometer. All measurements were done at room temperature. The Ar, N_2, and CH_4 gases (supplied by MG Scientific) have purities of 99.998%, 99.998%, and 99.99%, respective-

ly. SO_2 or CS_2 was diluted in Ar, N_2, or CH_4 before being introduced into the gas cell. The SO_2 supplied by Matheson has a purity of 99.98%. The CS_2 liquid with 99.9% purity was supplied by MCB Manufacturing Chemists, Inc. The CS_2 liquid contained in a stainless steel cylinder was pumped several hours at dry ice temperature to remove dissolved impurities before its vapor was used in the experiment. The impurity level was believed to be very low, because the experimental results were reproducible before or after an additional pumping. The impurities that possibly accompanied CS_2 vapor should not be more than 0.1%.

III. RESULTS AND DISCUSSION

A. SO_2

The waveforms of electron transient voltages for the SO_2–Ar mixture at $E/N = 2.5$ Td are shown in Fig. 1, where the pressure of Ar was 240 Torr, and the pressures of SO_2 were (a) 0, (b) 0.032, and (c) 0.082 Torr, respectively. The pulse was produced by a single shot, but it is a representative for the average of several sequential shots. From shot to shot, the pulse amplitudes varied within 10%. This variation was mainly caused by the fluctuation of laser energy. The curves shown in Fig. 1 were taken under the same experimental conditions.

As shown in Figs. 1(b) and 1(c), both the pulse durations and the amplitudes decreased when a small amount of SO_2 was admitted into the gas cell. The shortening of pulse duration is due to the increase of electron drift velocity, similar to the cases observed in the H_2O–Ar[17,21] and C_3F_8–Ar[18,22] mixtures. The decrease of amplitudes is caused by electron attachment to SO_2. This decrease of amplitude can be used to derive the electron attachment rate as described in previous papers.[16,17] The method of analysis of our data is briefly described below.

The electron conduction current induced by electron motion between the electrodes can be expressed as follows[23]:

$$i(t) = eN_e W/d ,\qquad (1)$$

where N_e is the number of electrons existing between the electrodes, W is the electron drift velocity, and d is the electrode spacing. When a small amount of SO_2 is added to the gas cell, the electron conduction current will decrease due to attachment, which becomes

$$i'(t) = eN'_e W'e^{-v_a t}/d ,\qquad (2)$$

where v_a is the electron attachment rate (or frequency). N'_e and W' may vary slightly from the values of Eq. (1). The transient voltage in Fig. 1 is related to the electron conduction current by

$$V(t) = f(t)i(t)R ,\qquad (3)$$

where R is the resistor connecting the anode to ground, and $f(t)$ is the electronics response function that approaches a constant at $t > RC$ (about 60 ns).

The logarithm of the ratio of the voltages with and without SO_2 in buffer gas is thus

$$\ln(V'/V) = \ln(N'_e W'/N_e W) - v_a t .\qquad (4)$$

At atmospheric pressure and relatively low values of E/N, electrons can reach an equilibrium state in a very short time.[17,23] Thus, W and W' can be practically considered as constant except for those electrons near the electrodes. For $T < d/W$ (or d/W'), N_e (or N'_e) is a constant except for the beginning of the pulse where some electrons diffuse back to the cathode.[23] Therefore, after a short period of time, the first term of Eq. (4) should be independent of time and the slope of $\ln(V'/V)$ vs time gives the electron attachment rate.

The electron attachment rate constant of the two-body process is determined by $v_a/[SO_2]$. In the SO_2–Ar mixture, we find that the $v_a/[SO_2]$ value is independent of Ar pressure and decreases with increasing $[SO_2]/[Ar]$, similar to the results reported by Rademacher et al.[8] This decrease is likely caused by the effect of SO_2 on the electron energy distribution in Ar, similar to the case of H_2O.[17] The electron attachment rate constant, k_a, which is obtained from extrapolating the plot of $v_a/[SO_2]$ vs pressure at $[SO_2] = 0$, is associated with the electron energy distribution of pure Ar. The results of the k_a values at various E/N are shown in Fig. 2 for an Ar pressure of 240 Torr. The scale of the mean electron energy, $\langle\epsilon\rangle$, is shown in the top of Fig. 2, where the $\langle\epsilon\rangle$ value in Ar was given by Christophorou and Hunter.[24] For comparison, the results of Rademacher et al.[8] are plotted as a solid line in Fig. 2, and the agreement between these two data is quite good.

The electron attachment in the SO_2–Ar mixture is mainly due to the dissociative attachment process,[8] for which SO_2 is dissociated into $SO + O^-$, $SO^- + O$, and $S^- + O_2$ whose threshold energies are 4.15, 4.52, and 3.6 eV,[3,5,8] respectively. As shown in Fig. 2, the electron attachment rate constant increases with increasing E/N.

The attachment rates of low-energy electrons to SO_2 in N_2 were measured at various E/N (0.5–3 Td). The values of $v_a/[SO_2]$ vs E/N and $\langle\epsilon\rangle$ are shown in Fig. 3, where $[N_2] = 490$ Torr and $[SO_2] = 0.4$–1.7 Torr. The values of $\langle\epsilon\rangle$ in N_2 as a function of E/N were given by Christophorou and Hunter.[24] In the SO_2 pressure range studied, the $v_a/[SO_2]$ values are not significantly affected by $[SO_2]$. As shown in Fig. 3, the $v_a/[SO_2]$ values decrease with increasing E/N. At E/N higher than 3 Td, the electron attachment rates are too small to be measured accurately.

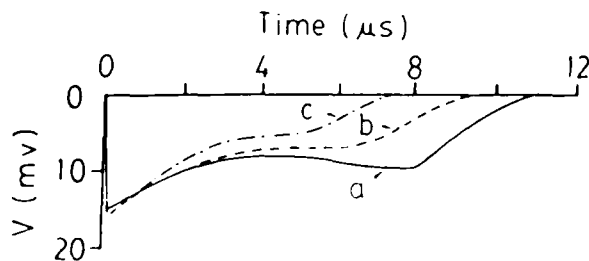The dependence of the $v_a/[SO_2]$ values on $[N_2]$ was investigated extensively by Rademacher et al.[8] for the N_2,
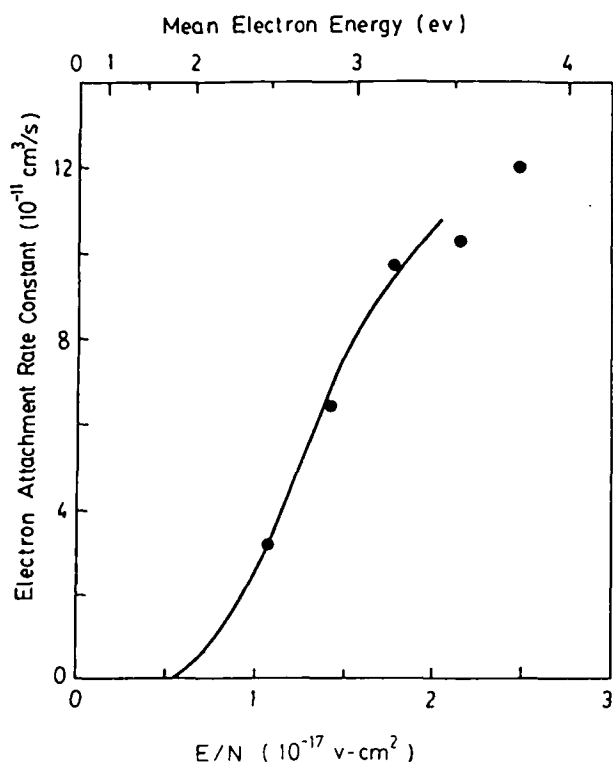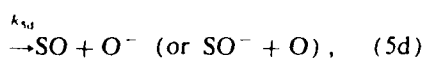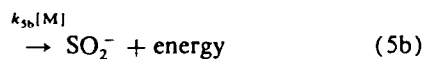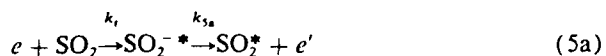

Time (μs)

FIG. 2. Electron attachment rate constant as a function of E/N (bottom scale) and mean electron energy (top scale) for SO_2 in Ar. The data from Ref. 8 (—) are plotted for comparison.

FIG. 3. The $\nu_a/[SO_2]$ values (•) as a function of E/N (bottom scale) and mean electron energy (top scale) for SO_2 (0.4–1.7 Torr) in 490 Torr of N_2. The data from Ref. 8 (—) which were taken at 500 Torr of N_2 are plotted for comparison.

pressure in the range of 300–23 000 Torr. The electron attachment rates (αW in Ref. 8) increase linearly with $[N_2]$ at pressures less than 4000 Torr, and they show saturation at higher pressures. The data with $[N_2] = 500$ Torr in Ref. 8 are plotted in Fig. 3 to compare with our data. As shown in Fig. 3, the agreement between these two data is again very good.

The values of $\nu_a/[SO_2]$ for the SO_2–CH_4 mixtures were measured as a function of E/N or $\langle \epsilon \rangle$ as shown in Fig. 4 for $[CH_4] = 257$ and 427 Torr. At each E/N, the $\langle \epsilon \rangle$ value is assumed to be equal to $3/2(eD_L/\mu)$, where D_L/μ is the ratio of lateral electron diffusion coefficient to electron mobility.[24] In this measurement, the SO_2 pressure was varied in the range of 0.4–1.7 Torr, and the observed $\nu_a/[SO_2]$ values did not depend on $[SO_2]$.

The electron attachment processes of SO_2 in various buffer gases have been explained[8] by the following processes:

$$e + SO_2 \xrightarrow{k_t} SO_2^{-*} \xrightarrow{k_{5a}} SO_2^* + e' \tag{5a}$$

$$\xrightarrow{k_{5b}[M]} SO_2^- + \text{energy} \tag{5b}$$

$$\xrightarrow{k_{5c}} SO_2^- + h\nu \tag{5c}$$

$$\xrightarrow{k_{5d}} SO + O^- \ (\text{or } SO^- + O) , \tag{5d}$$

where k_t is the rate constant for the formation of the "temporary" compound negative ion SO_2^{-*}, k_{5a} is the rate constant for autoionization, k_{5b} is the rate constant for the collisional

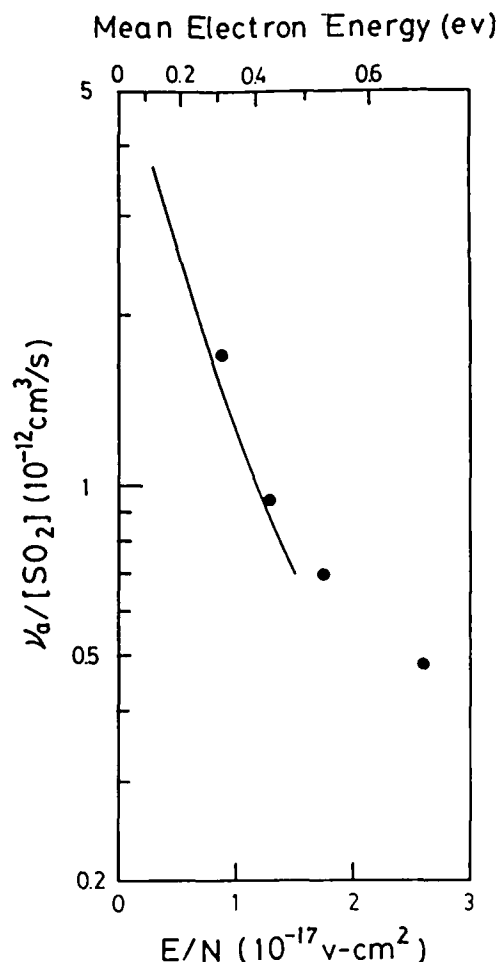stabilization of SO_2^{-*} by a third body M, k_{5c} is the rate constant for the radiative stabilization of SO_2^{-*}, and $k_{5d} f$ is the dissociative electron attachment rate constant.

For $\langle \epsilon \rangle > 2$ eV, the dissociative electron attachment process (5d) will occur as observed in the Ar buffer gas (see
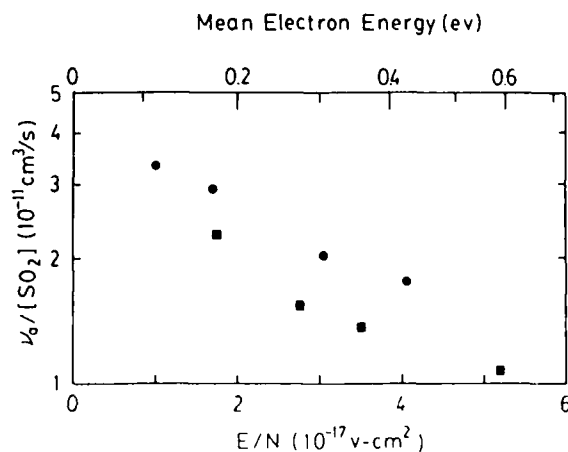

FIG. 4. The $\nu_a/[SO_2]$ as a function of E/N (bottom scale) and mean electron energy (top scale) for SO_2 (0.4–1.7 Torr) in 427 (•) and 257 (■) of CH_4

Fig. 2). For lower $\langle\epsilon\rangle$, only the processes (5a)–(5c) are possible. The third body M here could be either N_2, CH_4 (or C_2H_4 in Ref. 8), or even SO_2. The $[SO_2]$ dependence of $v_a/[SO_2]$ had been observed[5,6] before in pure SO_2 but not in this work and Refs. 7 and 8 whose SO_2 mixtures were used. Since the buffer gas pressures were about two orders of magnitude higher than $[SO_2]$ in this work, unless the k_{5b} with SO_2 as a third body is more than two orders of magnitude higher than those with the buffer gases, the collisional stabilization of SO_2^-* by SO_2 should be negligible here. The attachment rate derived from processes (5a)–(5c) is

$$v_a/[SO_2] = k_t(k_{5b}[M] + k_{5c})/(k_{5a} + k_{5b}[M] + k_{5c}) . \tag{6}$$

For the case[8] of C_2H_4, k_{5c} is much smaller than $k_{5b}[M]$, because $v_a/[SO_2] \to 0$ as $[C_2H_4] \to 0$. This may be also the case in CH_4. Thus, $v_a/[SO_2]$ can be approximated as

$$v_a/[SO_2] = k_t k_{5b}[M]/(k_{5a} + k_{5b}[M]) . \tag{7}$$

The k_t value will depend on $\langle\epsilon\rangle$. However, at low $\langle\epsilon\rangle$, it may not vary largely with $\langle\epsilon\rangle$. The k_t values[8] are 8.9×10^{-11} and 7.0×10^{-11} cm³/s for SO_2–N_2 in $0.04<\langle\epsilon\rangle<0.13$ eV and for SO_2–C_2H_4 in $0.041<\langle\epsilon\rangle<0.085$ eV, respectively. If we take the k_t value in SO_2–CH_4 to be equal to the value in SO_2–C_2H_4, the $v_a/[SO_2]$ value of 3.3×10^{-11} cm³/s measured at 427 Torr of CH_4 and $E/N = 1.0$ Td ($\langle\epsilon\rangle = 0.11$ eV) gives the ratio of $k_{5b}/k_{5a} = 2.1\times10^{-3}$ Torr^{-1} for CH_4 as a third body. This value is between the values[8] of 6.7×10^{-5} and 6.3×10^{-3} Torr^{-1} obtained from N_2 and C_2H_4, respectively. These results show that CH_4 is more effective than N_2 in stabilizing SO_2^-* to SO_2^-, but it is less effective than C_2H_4. This is consistent with the fact that large molecules have more degrees of freedom to take away the excess energy of SO_2^-*. This phenomenon is also observed in the electron attachment processes of CS_2 as described below.

B. CS_2

The transient waveforms of electron voltages with 0, 0.236, and 0.367 Torr of CS_2 in 250 Torr of N_2 are shown in Figs. 5(a), 5(b), and 5(c), respectively, where E/N is fixed at 5.1 Td. Again, the decrease in the electron voltages in Figs. 5(b) and 5(c) is due to the electron attachment to CS_2. The attachment rate v_a can be obtained from the ratio of the voltages with and without CS_2 in N_2.
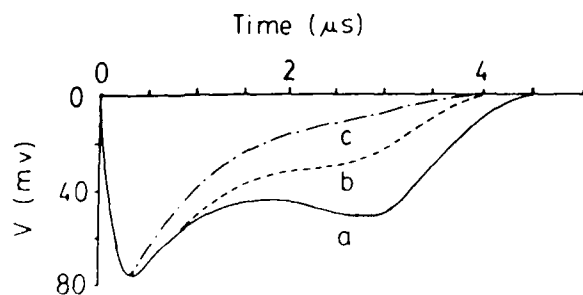
The $v_a/[CS_2]$ value for the CS_2–N_2 mixture is dependent on both $[CS_2]$ and $[N_2]$ in the gas cell, in contrast to the SO_2–N_2 mixture whose $v_a/[SO_2]$ value is only dependent on $[N_2]$. At a fixed $[N_2]$, it increases linearly with increasing $[CS_2]$ as shown in Fig. 6, where E/N is 9.64 Td and $[N_2]$ are 256, 371, 440, and 515 Torr. At each $[CS_2]$, the $v_a/[CS_2]$ value increases with increasing $[N_2]$. The intercepts of Fig. 6 are linearly dependent on $[N_2]$ as shown in Fig. 7.

The above results suggest that the electron attachment to CS_2 is explainable by processes (5a)–(5c), where SO_2 is replaced by CS_2. These processes are often used to explain the low-energy electron attachment to electronegative gases.[25] Since $v_a/[CS_2] \to 0$ as both $[CS_2] \to 0$ and $[N_2] \to 0$ as shown in Fig. 7, the k_{5c} in Eq. (6) is thus negligible when compared with $k_{5b}[M]$. Thus, only the processes (5a) and (5b), which are called the Bloch–Bradbury two-step three-body attachment processes,[19] are needed to explain our work in CS_2. In order to accommodate the results that $v_a/[CS_2]$ is linearly dependent on $[CS_2]$ and $[N_2]$, the k_{5a} in Eq. (6) (with $[SO_2]$ replaced by $[CS_2]$) must be larger than $k_{5b}[M]$. Taking these approximations into consideration, Eq. (6) (with $[SO_2]$ replaced by $[CS_2]$) simplifies to

$$v_a/[CS_2] = k_t k_{5b}[M]/k_{5a} . \tag{8}$$

It should be noted that for the case of CS_2, $[M]$ includes both $[CS_2]$ and $[N_2]$, because the stabilization rate of CS_2^-* by CS_2 is comparable with N_2 in the gas cell, namely,

$$v_a/[CS_2] = k_9[CS_2] + k_9'[N_2] . \tag{9}$$

A plot of $v_a/[CS_2][N_2]$ vs $[CS_2]/[N_2]$ at each E/N will give k_9 as the slope and k_9' as the intercept. The plots measured at various E/N (2.55–16.7 Td) are shown in Fig. 8, from which the values of k_9 and k_9' are determined and are
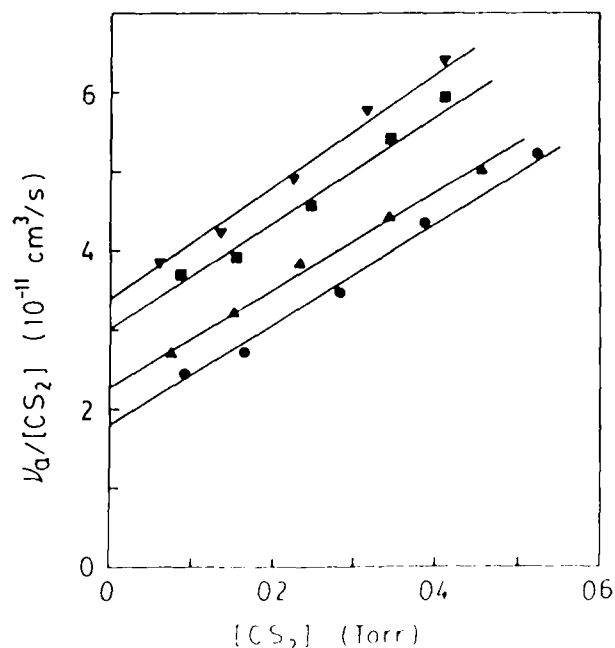

Time (μs)

FIG. 5. The waveforms of transient voltage pulses produced from the electron motion in 255 Torr of N_2 as without CS_2, b) with 0.236 Torr, and (c) with 0.367 Torr of CS_2. The E/N was fixed at 5.1 Td. The electrode spacing was 3.6 cm, and the external resistance was 2 kΩ.

FIG. 6. The $v_a/[CS_2]$ values as a function of $[CS_2]$ for $[N_2]$ = 256 (●), 371 (▲), 440 (■), and 515 (▼) Torr, respectively. The E/N was fixed at 9.64 Td. The straight lines are drawn to fit the data points.
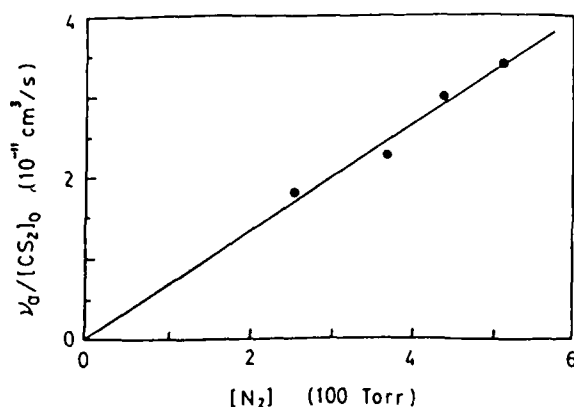
FIG. 7. The intercepts, $\nu_a/[SO_2]_0$, of the lines in Fig. 6 at $[CS_2] = 0$ as a function of N_2 pressure.

plotted as a function of E/N in Figs. 9(a) and 9(b), respectively. k_9 is about three orders of magnitude higher than k'_9, indicating that CS_2 is much more effective than N_2 to stabilize CS_2^{-*}.

The electron attachment to CS_2 in CH_4 was also studied in this experiment. Similar to the CS_2–N_2 mixture, at a fixed $[CH_4]$, the $\nu_a/[CS_2]$ values increase linearly with increasing $[CS_2]$ as shown in Fig. 10, where E/N was fixed at 10.1 Td and $[CH_4]$ were 146, 255, 390, and 525 Torr. The intercepts of the linear lines of $\nu_a/[CS_2]$ vs $[CS_2]$ in Fig. 10 increase linearly with increasing $[CH_4]$, similar to the case of N_2 (See Fig. 7).

Again, the $\nu_a/[CS_2]$ values for the CS_2–CH_4 mixture can be expressed by

$$\nu_a/[CS_2] = k_{10}[CS_2] + k'_{10}[CH_4] . \tag{10}$$

FIG. 9. Three-body attachment rate constants k_9 and k_{10} of CS_2 with CS_2 as a third body in N_2 (a) and CH_4 (c), and k'_9 with N_2 (b) and k'_{10} with CH_4 (d) as a third body as a function of E/N.

The plot of $\nu_a/[CS_2][CH_4]$ vs $[CS_2]/[CH_4]$ at each E/N will give k_{10} and k'_{10}. These plots for various E/N the range of 3.39 to 16.79 Td are shown in Fig. 11. These k_{10} and k'_{10} values derived from Fig. 11 are plotted in Figs. 9(c) and 9(d). At each E/N, k_{10} is about two orders of magnitude higher than k'_{10}. Similar to the CS_2–N_2 case, CS_2 is also much more effective than CH_4 as a third body in stabilizing CS_2^{-*}.

CS_2^- is a stable molecule because of its positive electron affinity (about 0.5–1 eV[11,12]). CS_2^- has been observed in several experiments, although a direct attachment of low-energy electron to CS_2 has not yet been reported. In the stud-

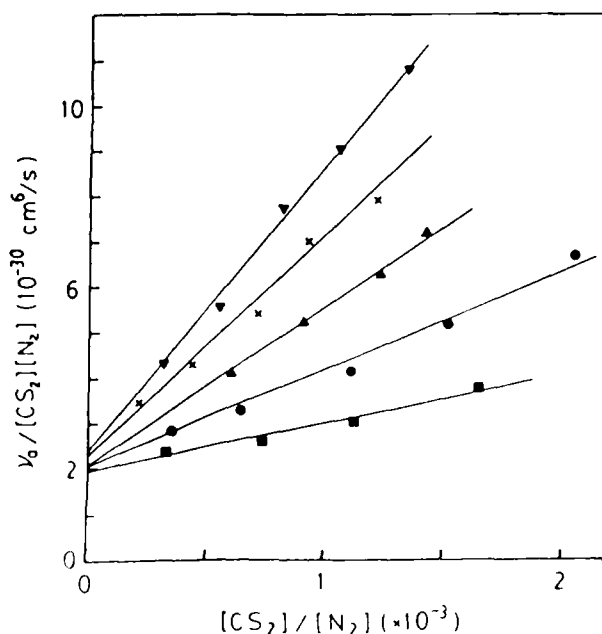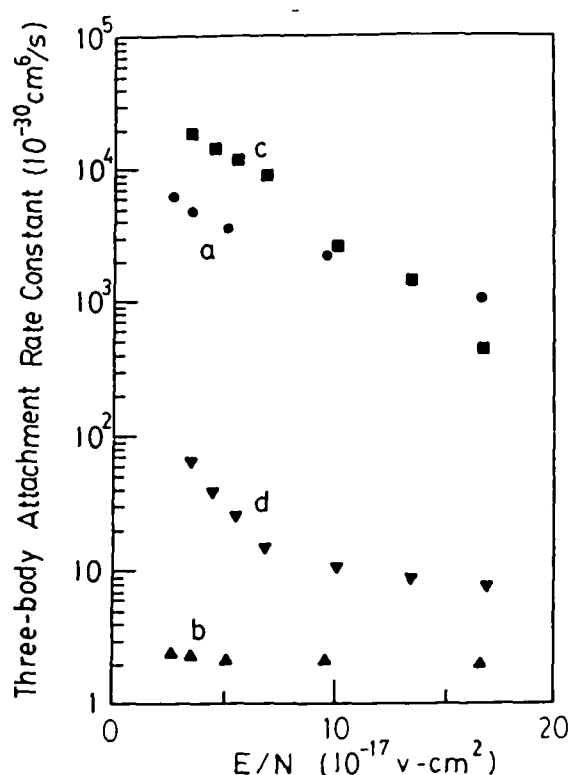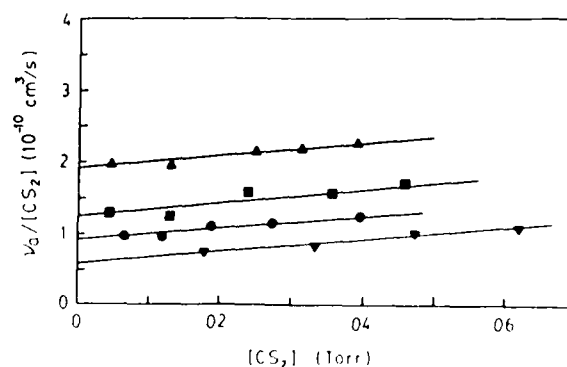FIG. 11. Three-body attachment rate constant $\nu_a/[CS_2][N_2]$ as a function of $[CS_2]/[N_2]$, where $[N_2]$ was fixed at 255 Torr, and $E/N = 2.55$ (▼), 3.4 (×), 5.1 (▲), 9.64 (●), and 16.7 (■) Td, respectively.

FIG. 10. The $\nu_a/[CS_2]$ values as a function of $[CS_2]$ at $E/N = 10.1$ Td, and $[CH_4] = 146$ (▼), 255 (●), 390 (■), and 525 (▲) Torr.

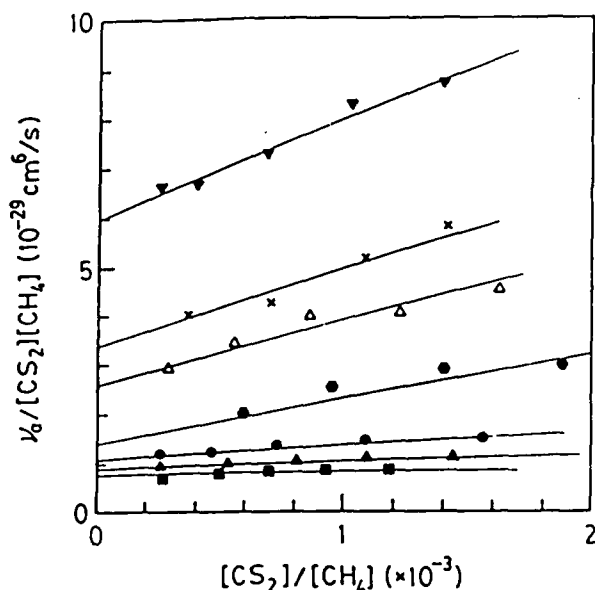FIG. 11. Three-body attachment rate constant $v_a/[CS_2][CH_4]$ as a function of $[CS_2]/[CH_4]$ at $[N_2] = 255$ Torr and $E/N = 3.39$ (▼), 4.42 (×), 5.43 (△), 6.77 (○), 10.1 (●), 13.45 (▲), and 16.79 (■) Td.
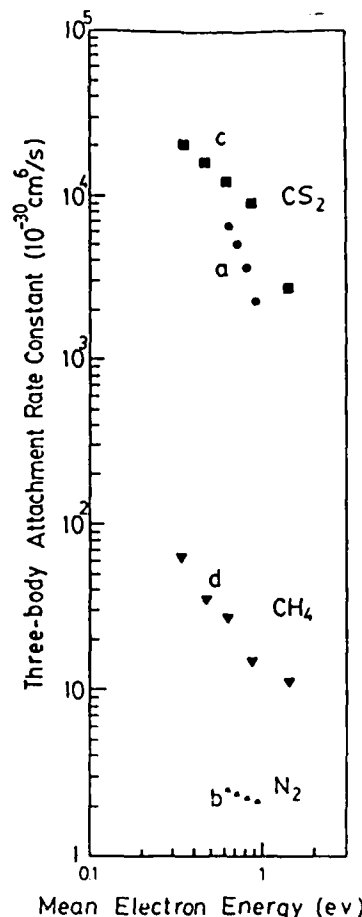

FIG. 12. Three-body attachment rate constants, k_9 and k_{10} of CS_2 with CS_2 as a third body in N_2 (a) and CH_4 (c), and k'_9 with N_2 (b) and k'_{10} with CH_4 (d) as a third body as a function of mean electron energy.

ies of the dissociative electron attachment process of CS_2 (the energy threshold is about 3 eV)[13,15,26]. CS_2^- as well as C^-, S^-, CS^-, and S_2^- have been observed.[13-15] The observed CS_2^- ion was attributed to the secondary charge transfer process, possibly by $CS_2 + CS^- \rightarrow CS_2^- + CS$. CS has an electron affinity comparable with CS.[15,26] The CS_2^- ion was also observed in the collisional ionization of Na, K, and Cs,[12] namely, (Na, K, Cs) + $CS_2 \rightarrow$ (Na$^+$, K$^+$, Cs$^+$) + CS_2^-. CS_2^- was also observed in the reaction of CS_2 with Kr** in highly excited Rydberg states. Such a highly excited Kr atom has a similar characteristic to a free slow electron,[12] i.e., Kr** + $CS_2 \rightarrow$ Kr$^+$ + CS_2^-. CS_2^- was also observed in the charge transfer from several negative ions[11] (O$^-$, Cl$^-$, and S$^-$).

The mean electron energy in N_2 or CH_4 is so low (< 1.5 eV) that the dissociative attachment process is not energetically possible. The electron attachment observed in this experiment must be due to the three-body process which is explained by the two-step processes. Our results show that the efficiencies of CS_2, N_2, and CH_4 in stabilizing the CS_2^-* ion are quite different as shown in Fig. 12. The three-body attachment rate constants k_9 and k_{10} for CS_2 as a third body, and k'_9 and k'_{10} for N_2 and CH_4 as third bodies are plotted vs the mean electron energy $\langle\epsilon\rangle$ in Fig. 12. CS_2 is about two orders of magnitude more efficient than CH_4 for the stabilization of CS_2^-*. The efficiency of CH_4 in stabilizing CS_2^-* is about one order of magnitude higher than that of N_2. This is similar to the SO_2 case where CH_4 is also about one order of magnitude more efficient than N_2 in stabilizing SO_2^-*. This may be due to the fact that CH_4 has more degrees of freedom than N_2 so that CH_4 is a better quencher in that it is able to carry away the excess energy of CS_2* more effectively.

It is surprising to see that CS_2 is so much more efficient to stabilize CS_2^-* than CH_4. There may be an accidental resonance between the states of CS_2* and CS_2 such that the

energy transfer process occurs very fast. There is another possibility CS_2^- may be from a charge transfer process such as CS_2^-* + $CS_2 \rightarrow CS_2^*$ + CS_2^-, instead of a collisional stabilization such as CS_2^-* + $CS_2 \rightarrow CS_2^-$ + CS_2 + energy. At each $\langle\epsilon\rangle$, the values of k_9 and k_{10} should be the same, because these rate constants only associate with CS_2. However, they show a discrepancy in Fig. 12. The discrepancy could be due to the fact that the $\langle\epsilon\rangle$ in CH_4 is not appropriately determined from E/N. The assumption of the Maxwell function for the electron energy distribution in CH_4 used to determine $\langle\epsilon\rangle = 3/2(eD_L/\mu)$ may not be quite appropriate.

The anomalous pressure dependence of the electron attachment had been observed in dense gases. For O_2 and N_2O, for instance, their high electron attachment rates at high buffer gas pressure were not consistent with the results predicted by the Bloch–Bradbury mechanism. Hatano and Shimomori[28] proposed that the electron attachment to van der Waals molecules plays an important role in those O_2 and N_2O cases. Recently, Hunter et al.[29] observed that electron attachment to 1-C_3F_6 was dependent on 1-C_3F_6 pressure. They attributed this to be the clusterization of the transient parent anion. The above electron attachment mechanism may also be one of the reasons that causes the unusual CS_2 pressure dependence observed in this work. That is, the electron attachment in CS_2 may be by the pre-existing dimer molecules of CS_2 or by the dimerization of the transient parent anion, i.e.,

$$CS_2^- {}^* + CS_2 \rightarrow (CS_2)_2^- {}^* \xrightarrow{[M]} (CS_2)_2^- + energy \, .$$
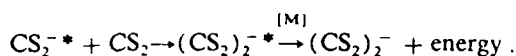
The electron attachment rate for the CS_2–Ar mixture was also studied in this experiment. However, at low $[CS_2]$, the attachment rates were too small to be measured within the experimental certainty. This is due to the fact that the dissociative attachment cross section of CS_2 is quite low[27] (one order of magnitude less than that of SO_2). It requires very high $[CS_2]$ in order to observe a sufficient attachment rate. In this case, the breakdown starts to occur and the transient voltage is disturbed by the noise associated with prebreakdown phenomena.

IV. CONCLUSION

A parallel-plate drift-tube electron-swarm technique is applied to measure the low-energy electron attachment rate constants of SO_2 and CS_2 in the buffer gases of Ar, N_2, and CH_4 at various E/N. For SO_2 in Ar and N_2, our results are consistent with the published data.[8] New data are obtained for SO_2 in CH_4 and CS_2 in N_2 and CH_4. Both the low-energy electron attachment to SO_2 and CS_2 in N_2 and CH_4 are attributed to the Bloch–Bradbury two-step three-body attachment process. The relative effectiveness of N_2, CH_4, CS_2, and SO_2 as third bodies in the three-body attachment process are also determined from the measured attachment rate constants.

ACKNOWLEDGMENTS

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Appendix B

Electron Attachment Rate Constants of

$SOCl_2$ in Ar, N_2, and CH_4

Electron Attachment Rate Constants of $SOCl_2$ in Ar, N_2, and CH_4

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ABSTRACT

The electron attachment rate constants of $SOCl_2$ in the buffer gases of Ar, N_2, and CH_4 (150 to 500 Torr) at various E/N (1-15 Td) were measured by a parallel-plate drift-tube electron-swarm technique. Electrons were produced by irradiating the cathode with KrF laser photons. For the $SOCl_2$-Ar mixture, the electron attachment rate constant has a maximum value of 1.2×10^{-10} cm^3/s at E/N = 4 Td. For $SOCl_2$ in N_2, the electron attachment rate constant is 2.5×10^{-9} cm^3/s at E/N = 1.3 Td, and decreases with increasing E/N. For $SOCl_2$ in CH_4, the electron attachment rate constant is 9.5×10^{-9} cm^3/s at E/N = 1 Td, and decreases with increasing E/N. For every gas mixture studied, the electron attachment rate constant is independent of buffer gas pressure, indicating that the electron attachment to $SOCl_2$ is due to a dissociative process. The electron attachment processes in the three gas mixtures are discussed.

I. INTRODUCTION

Recently, we have observed that the conduction current in a glow discharge of the $SOCl_2$-N_2 mixture could be reduced when the gas medium was irradiated by ArF laser photons. The current reduction may be caused by the enhancement of electron attachment due to the Cl and SO radicals, where these radicals are produced from the photodissociation of $SOCl_2$ by ArF laser photons. This result indicates that $SOCl_2$ could be useful for the development of laser controlled opening switches. The electron attachment rates for $SOCl_2$ in various buffer gases are the basic information needed for such application. Such need motivates us to do this investigation.

A parallel-plate drift-tube electron-swarm technique has been used in our laboratory to measure the electron attachment rate constants of several molecules.[1-4] The electron attachment rate constants of $SOCl_2$ in Ar, N_2, and CH_4 at varied E/N are reported in this paper. These data are not yet available in the literature. The electron attachment processes of $SOCl_2$ in various buffer gases are discussed based on the experimental data measured.

II. EXPERIMENT

The experimental set-up was described in previous papers.[1-4] In brief, the gas cell was a 6 in. six-way aluminum cross. The electrodes were two parallel uncoated stainless steel plates 5 cm in diameter and 3 cm apart. The electron swarm was produced by irradiation of the cathode with a KrF (Lumonics model 861S) laser

beam which had a pulse duration of about 10 ns. These photons, of wavelength 248 nm ($\sim$5.0 eV), are energetically capable of dissociating $SOCl_2$.[5,6] In order to minimize the interference of the $SOCl_2$ electron attachment measurement by photofragments such as SO, Cl, and Cl_2, the size of the laser beam was reduced to 0.3 cm radius such that only a small fraction of $SOCl_2$ between the electrodes was irradiated by laser photons. (This arrangement confines the photofragments to a small region around the cathode.) In the data analysis (see next section), only electron motion in the region far away from the cathode was considered. This way of data analysis ensures that the electron attachment rate measured is due to $SOCl_2$ only.

A negative high voltage was applied to the cathode to maintain an electric field between the electrodes. The conduction current induced by the electron motion between the electrodes was observed as a transient voltage pulse across a resistor (330-2000 Ω) connecting the anode to ground. The trace of each transient pulse was monitored by a 150 MHz digital storage oscilloscope (Tektronix 2430) and was subsequently stored in an IBM XT microcomputer; data were analyzed by the computer.

Pressure in the gas cell was kept constant as monitored by an MKS Baratron manometer while a slow flow of gas, 20 cm^3/min, was maintained. All measurements were at room temperature, C. All gases were supplied by MG Scientific and were used as received; purities of the Ar, N_2, and CH_4 were better than 99.998%, 99.998%, and 99.99%, respectively. Thionyl chloride was supplied by Fisher Scientific and was of 99% purity.

The thionyl chloride liquid is stored in a glass bottle

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inside a stainless steel container. The thionyl chloride vapor was carried from the container into the gas cell by the buffer gas, Ar, N_2, or CH_4. The concentration of $SOCl_2$ was determined from the ratio of $SOCl_2$ vapor pressure (110 Torr at 23°C) and carrier gas pressure (2 atm). The measurements were also done by pre-mixed $SOCl_2$ in various buffer gas. These mixtures had well defined concentrations of $SOCl_2$. Results obtained by using different methods of mixing gases did not differ. The major dissolved impurity in $SOCl_2$ has been reported to be SO_2,[7] however, the attachment rate constant for SO_2 is much smaller than that for $SOCl_2$, so the effect of possible SO_2 impurity on these measurements should be negligible.

III. RESULTS

A. $SOCl_2$-Ar Mixture

The electron transient waveforms for the $SOCl_2$-Ar mixture at $E/N = 0.26$ Td (1 Td = 10^{-17} V cm^2) are shown in Fig. 1, where the pressure of Ar was 390 Torr, and the pressures of $SOCl_2$ were (a) 0, (b) 23, and (c) 50 mtorr. Each waveform is the average of 64 pulses which were captured by the digital storage oscilloscope. As can be seen from Fig. 1 (a) (with only Ar in the gas cell), voltage decreased rapidly after the first peak. This is probably due to the loss of electrons by back diffusion to the cathode.[8] After the peak, the voltage approached a nearly constant value until the electrons arrived at the anode, where the voltage dropped to zero. When small amounts of $SOCl_2$ were added to the gas cell, both pulse duration and amplitude decreased as shown in

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Fig. 1 (b) and (c). This decrease is caused by the electron attachment to $SOCl_2$.

The electron attachment rate ν_a at a fixed $SOCl_2$ concentration is obtained from the ratio of transient voltages as a function of time with and without $SOCl_2$. The method of data analysis has been described in detail elsewhere.[1,2] In the data analysis, only the flat portion of the trace was used for the rate measurement (the first peak was avoided). For example, the ratios for the voltages in Fig. 1 were considered only from t=2 to 4 μs. At this laster time, the conduction electrons are far away from the region irradiated by laser, so the possible interference by the Cl and SO radicals (which may be produced by photodissociation of KrF laser photons) is avoided. Thus, the measured electron attachment rates were caused by $SOCl_2$ only.

The electron attachment rate does not depend on the pressure. This shows that the electron attachment is a two-body dissociative process. The electron attachment rate constant k_a of the two-body process is determined by $\nu_a/[SOCl_2]$. Values of k_a measured at various E/N are shown in Fig. 2 for an Ar pressure of 390 Torr along with a scale of the mean electron energy,[9,10] $<\varepsilon>$. The electron attachment rate constant reaches a maximum value of 1.2×10^{-9} cm^3/s at E/N = 4 Td ($<\varepsilon>$ = 4.5 eV). The electron attachment rate constants were also measured at different Ar pressures and the results are the same as that shown in Fig. 2.

B. $SOCl_2$-N_2 Mixture

The measured electron attachment rate does not depend on the N_2 pressures from 150-500 Torr. This shows that the electron

attachment is a two-body dissociative process. The measured values of k_a, in the $SOCl_2-N_2$ mixture for E/N from 1 to 8 Td, are shown in Fig. 3, where the N_2 pressure is about 475 Torr. A scale of mean electron energy[9] in N_2 is also shown on the top axis of Fig. 3. The attachment rate constant is about 2.5×10^{-9} cm^3/s at E/N = 1.3 Td ($<\varepsilon> = 0.4$ eV), and decreases with increasing E/N.

C. $SOCl_2-CH_4$ Mixture

Similar to results obtained in Ar and N_2 buffer gases, the electron attachment rate does not depend on the CH_4 buffer pressure (varied from 150-500 Torr), indicating that the electron attachment is a two-body dissociative process. The electron attachment rate constants for the $SOCl_2-CH_4$ mixture are shown in Fig. 4 for E/N from 1 to 15 Td and for two different pressures of CH_4. The mean electron energies[9] in CH_4 are shown on the top axis of Fig. 4. (The mean electron energy in CH_4 for E/N higher than 12 Td is not available). As shown in Fig. 4, the attachment rate constant is about 9.5×10^{-9} cm^3/s at E/N = 1 Td ($<\varepsilon> = 0.1$ eV) and decreases with increasing E/N.

IV.   DISCUSSION

The electron attachment rate constants of $SOCl_2$ for the $SOCl_2-Ar$ and $SOCl_2-N_2$ mixtures are replotted against the mean electron energy as shown in Fig. 5. The attachment rate constant has a peak at the thermal energy and a broad band with a maximum at 4.8 eV. This result indicates that the electron attachment is due to at least two different dissociative attachment processes. (Note that the attachment is attributed to

a dissociative process because the attachment rate is independent of the buffer gas pressure). The attachment process at the thermal energy has an attachment rate higher than other processes.

The electron attachment rate measured in the $SOCl_2-CH_4$ mixture is higher than that measured in the $SOCl_2-N_2$ mixture at the same value of $<\varepsilon>$ (see Figs. 3 and 4). This difference could be due to the fact that $<\varepsilon>$ in CH_4 is not appropriately converted from E/N. The assumption of the Maxwell function used to determine the electron energy distribution in CH_4 as $<\varepsilon> = 3(e D_L/\mu)/2$ may not be correct. On the other hand, the electron energy distributions in Ar and N_2 have been well studied.[9,11] The electron attachment rate constants in the $SOCl_2-N_2$ and $SOCl_2-Ar$ mixtures match very well, as shown in Fig. 5. A similar case was observed for CS_2,[4] whose three-body electron attachment rate constant, measured in the CS_2-CH_4 mixture, was higher than that measured in the CS_2-N_2 mixture at same $<\varepsilon>$.

When $SOCl_2$ is excited by photons or electrons, it may be dissociated into the following products,

$$SOCl_2 \rightarrow Cl_2 + SO \qquad (1)$$
$$\rightarrow Cl + SOCl \qquad (2)$$
$$\rightarrow 2Cl + SO \qquad (3)$$

The thresholds for the above processes can be determined from their dissociation energies. The dissociation energy for D(Cl-SOCl) was calculated by Sanderson[12] to be 2.86 eV. The dissociation energy for D(SO-2Cl) is 4.70 eV.[13] Using D(Cl-Cl) = 2.52 eV,[13] the dissociation energy for D(SO-Cl$_2$) is 2.18 eV.

The thermochemical energies for the electron dissociative

attachment processes of $SOCl_2$ can be calculated from the dissociation energies as follows:

$$SOCl_2 + e \rightarrow SO^- + 2Cl - 3.6 \ eV \tag{4}$$

$$\rightarrow SO^- + Cl_2 - 1.1 \tag{5}$$

$$\rightarrow Cl^- + Cl + SO - 1.0 \tag{6}$$

$$\rightarrow Cl_2^- + SO + 0.0 \tag{7}$$

$$\rightarrow Cl^- + SOCl + 0.8 \tag{8}$$
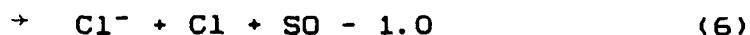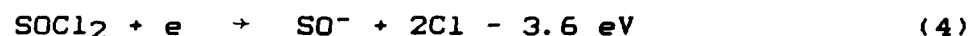
The electron affinities[9] of Cl, SO, and Cl_2 used in the calculation are 3.67, 1.1, and 2.2 eV, respectively. The calculated energy thresholds for all these possible dissociation processes and dissociative attachment processes of $SOCl_2$ are shown in Fig. 6.

The energy threshold of $SOCl + Cl^-$ is about 0.8 eV below the ground state energy of $SOCl_2$, indicating that the electron dissociative attachment could occur at thermal energy. This explains our observation that the electron attachment is a two-body dissociative process with a high attachment rate constant at low electron energy. The $Cl_2^- + SO$ process also requires no electron energy to occur, except for the possible potential barrier. Since process (8) has a high exothermic energy and the electron energy in the buffer gas CH_4 or N_2 is low, process (8) is probably the main electron attachment process occurring in the $SOCl_2-CH_4$ and $SOCl_2-N_2$ mixtures. A Similar case was observed in the Cl_2-N_2 mixture by McCorkle et al.[14], where the electron dissociative attachment rate constant has a maximum at $<\epsilon> \sim$ 0.07 eV and decreases with increasing $<\epsilon>$. The attachment rate constant for the $SOCl_2-CH_4$ mixture at $<\epsilon> \sim$ 0.1 eV measured in

this experiment is much higher than that in the Cl_2-N_2 mixture.[14] This is expected from the fact that the molecular size of $SOCl_2$ is larger than Cl_2. In fact it has been observed[10] that the electron attachment rate constants of perfluoroalkane molecules increase with increasing size.

The electron attachment rate constants of $SOCl_2$ increase when $<\varepsilon> > 1$ eV as shown in Fig. 5. This increase is probably caused by the dissociative attachment processes (4)-(6). The processes (7) and (8) are responsible for the attachment at the thermal energy and they will be less important at high electron energy. This is evident by the fact that the thermal electron peak rapidly decreases with increasing electron energy. Because energy thresholds for the processes (5) and (6) are about 1 eV above the ground state of $SOCl_2$, these processes are likely responsible for the electron attachment at electron energy higher than 1 eV. For electron energy higher than 3.6 eV, the process (4) will provide additional attachment channel to enhance the attachment rate. For electron energy higher than 4.8 eV, the attachment rate constant starts to decrease, which may be caused by the electron energy moving away from the energy range where the attachment processes are available. The next high energy process is $Cl_2^- + S + O$ whose energy threshold is 5.3 eV, where $D(S-O) = 5.34$ eV[13] is used to determine the threshold.

V. CONCLUSION

Electron attachment rate constants of $SOCl_2$ in Ar, N_2, and CH_4 were measured at various E/N (or mean electron energy). The electron attachment rate constant has a maximum at the thermal

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energy and a second maximum peak around 4.5 eV. The dissociative attachment processes of $Cl^- + SOCl$ and $Cl_2^- + SO$ are likely to be the dominant processes for the low energy electrons. For the high energy electrons, the dissociative attachment processes of $Cl^- + Cl + SO$, $SO^- + Cl_2$ and $2Cl + SO^-$ become important.

ACKNOWLEDGEMENT

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FIGURE CAPTIONS

Fig. 1   The waveforms of transient voltage pulses produced from electron motion in 390 Torr of Ar with $SOCl_2$ (a) 0, (b) 23 mTorr, and (c) 50 mTorr. Electrons were produced from irradiation of the cathode by KrF laser photons. The E/N was fixed at 0.26 Td. The electrode spacing was 3 cm, and the external resistor was 1 KΩ.

Fig. 2   Electron attachment rate constant as a function of E/N (botton axis) and mean electron energy (top axis) for $SOCl_2$ in Ar. The Ar pressure was 325 Torr.

Fig. 3   Electron attachment rate constant as a function of E/N (bottom axis) and mean electron energy (top axis) for $SOCl_2$ in N_2. The N_2 pressure was 475 Torr.

Fig. 4   Electron attachment rate constant as a function of E/N (bottom scale) and mean electron energy (top scale) for $SOCl_2$ in CH_4. The CH_4 pressures were 340 Torr (●) and 490 Torr (▲).

Fig. 5   Electron attachment rate constant as a function of mean electron energy for the $SOCl_2$-N_2 (▲) and $SOCl_2$-Ar (●) mixtures.

Fig. 6   Energy thersholds for the dissociation processes (left) and the electron dissociative attachment processes (right) of $SOCl_2$.
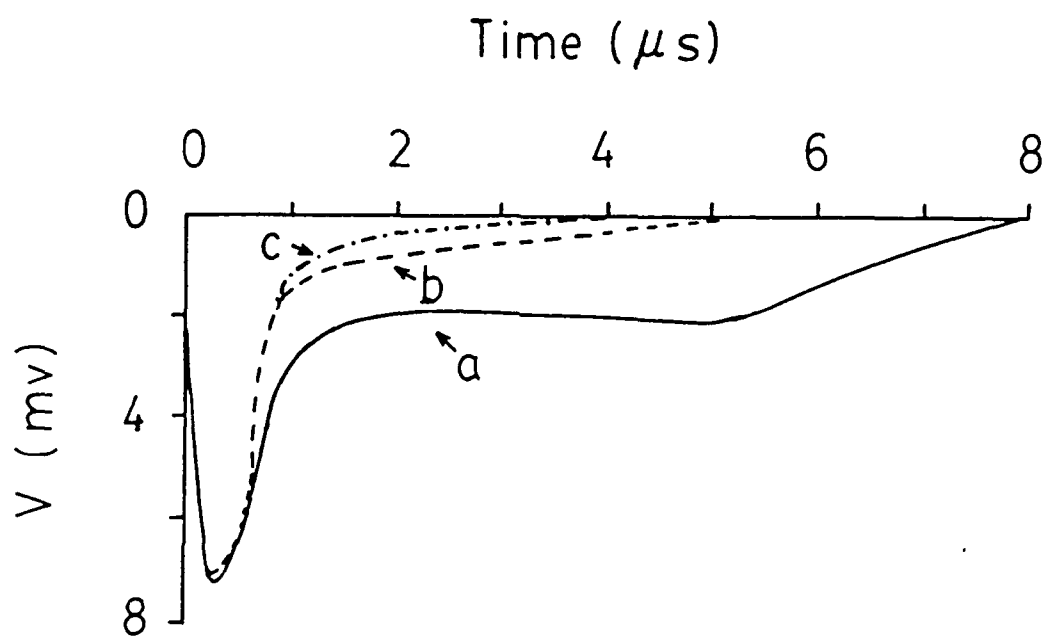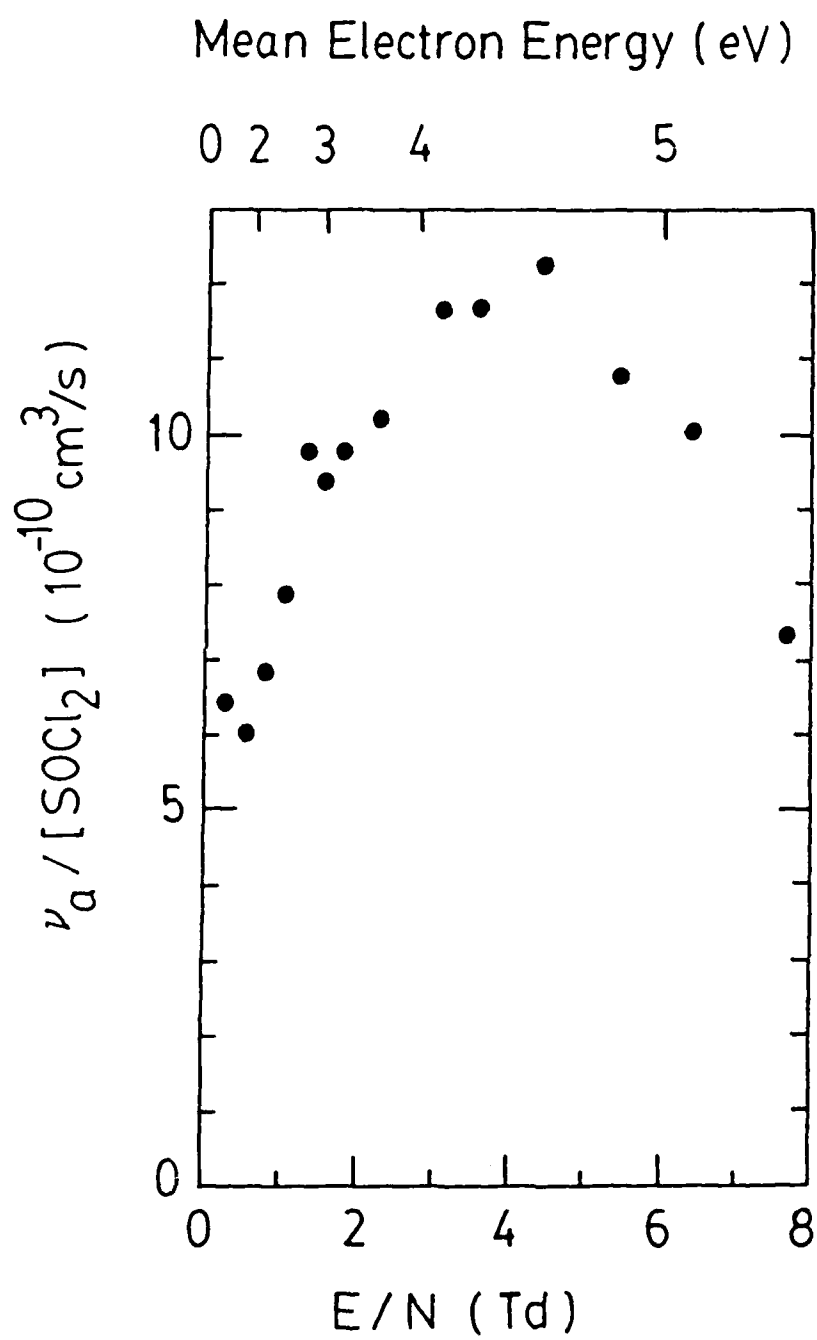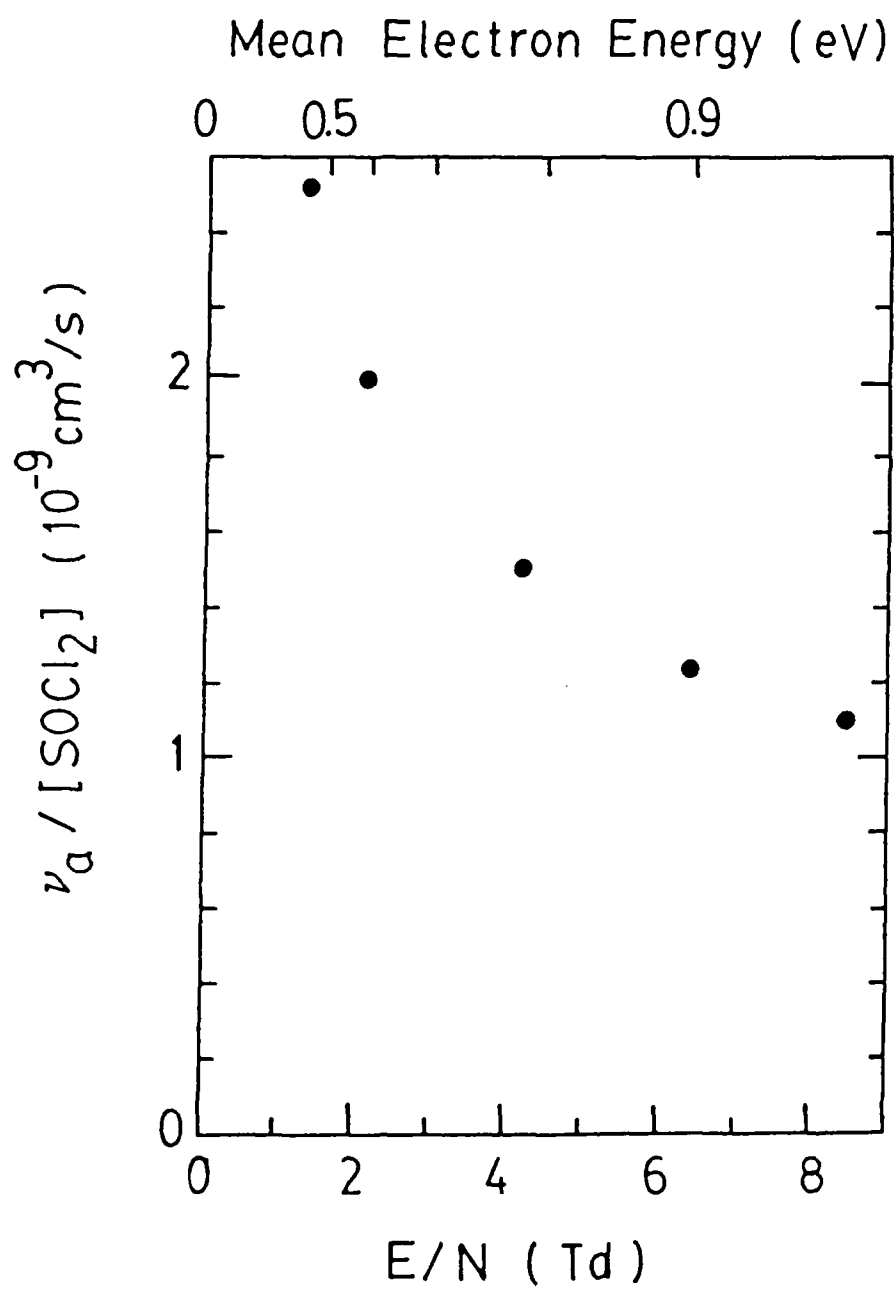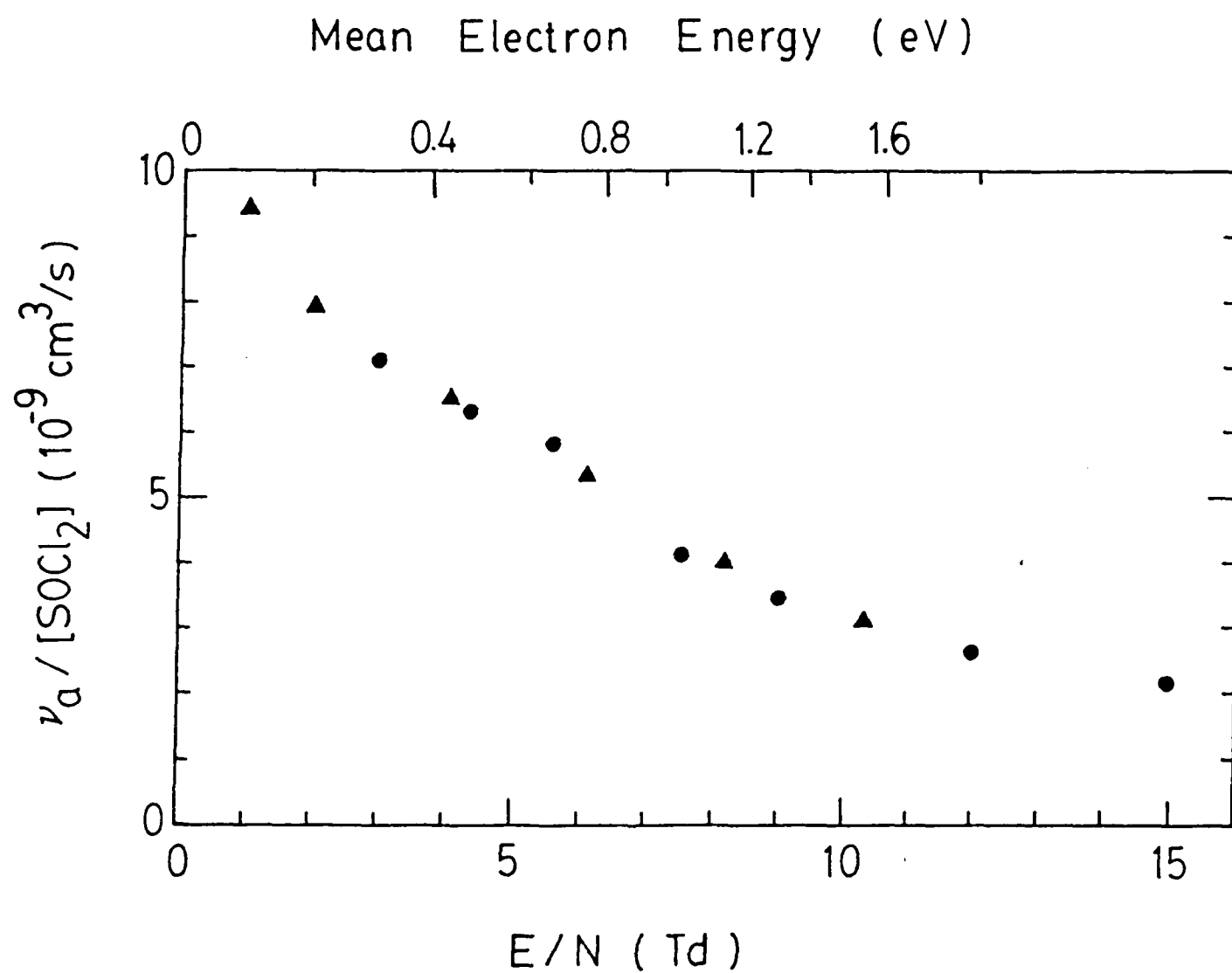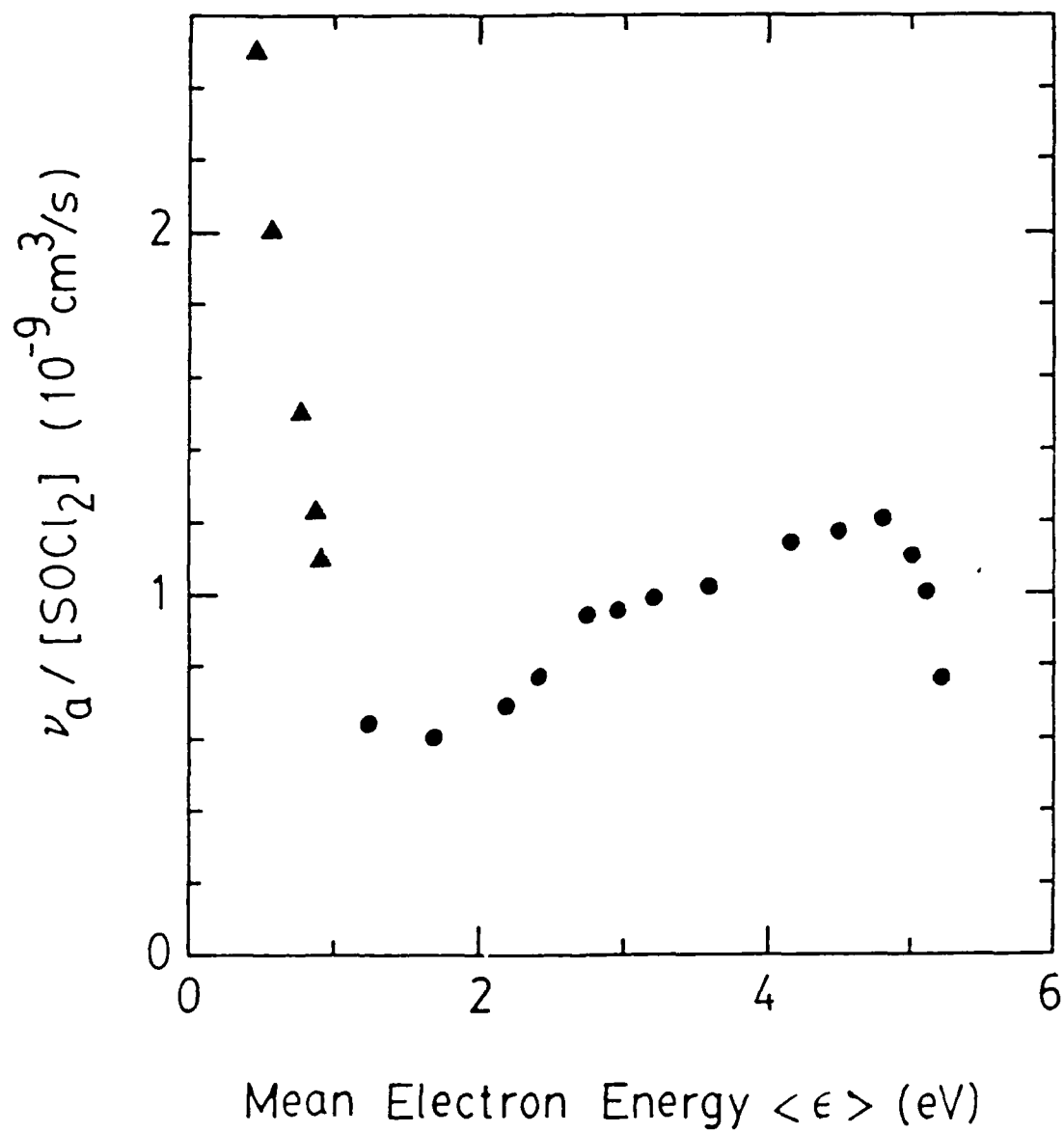
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Fig. 1

Mean Electron Energy (eV)

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

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